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RELATION BETWEEN FLOW AND TEMPORAL VARIATIONS OF NITRATE AND PESTICIDES IN TWO KARST SPRINGS IN NORTHERN ALABAMA[1]

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ABSTRACT: Two karst springs in the Mississippian Carbonate Aquifer of northern Alabama were sampled between March 1999 and March 2001 to characterize the variability in concentration of nitrate, pesticides, selected pesticide degradates, water temperature, and inorganic constituents. Water temperature and inorganic ion data for McGeehee Spring indicate that this spring represents a shallow flow system with a relatively short average ground-water residence time. Water issuing from the larger of the two springs, Meridianville Spring, maintained a constant temperature, and inorganic ion data indicate that this water represents a deeper flow system having a longer average ground-water residence time than McGeehee Spring. Although water-quality data indicate differing short-term responses to rainfall at the two springs, the seasonal variation of nitrate and pesticide concentrations generally is similar for the two springs. With the exception of pesticides detected at low concentrations, the coefficient of variation for most constituent concentrations was less than that of flow at both springs, with greater variability in concentration at McGeehee Spring. Degradates of the herbicides atrazine and fluometuron were detected at concentrations comparable to or greater than the parent pesticides. Decreases in concentration of the principal degradate of fluometuron from about July to November indicate that the degradation rate may decrease as fluometuron (demethylfluometuron) moves deeper into the soil after application. Data collected during the study show that from about November to March when recharge rates increase, nitrate and residual pesticides in the soil, unsaturated zone, and storage within the aquifer are transported to the spring discharges. Because of the increase in recharge, fluometuron loads discharged from the springs during the winter were comparable to loads discharged at the springs during the growing season.

(KEY TERMS: karst hydrology; pesticides; nitrate; pesticide degradates; water quality; monitoring.)

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INTRODUCTION

The susceptibility to contamination from surface sources and the dynamic flow and water-chemistry changes that can occur in karst ground-water systems are well documented (Quinlan, 1989; Scanlon, 1990; Currens, 1999). The variation in flow and water quality in karst springs is dependent on the relative extent to which conduit *vs*. diffuse flow dominates the

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spring discharge (Shuster and White, 1971; Jacobson and Langmuir, 1974). Variation in concentrations of contaminants over time in karst aquifers is also a function of the pathway that contaminants follow into the aquifer. Contaminants that are transported to ground water predominantly through direct flow paths from the surface (for example, sinkholes) may increase in concentration after rainfall before decreasing to prestorm levels. Conversely, contaminants that move through the soil and unsaturated zone into ground water may decrease in concentration for some time as a result of dilution shortly after rainfall. The most dramatic examples of variability in karst systems have been from springs dominated by conduit flow, where the natural water quality and the concentrations of contaminants can be affected greatly by rapid movement of rainfall into the subsurface (Ryan and Meiman, 1996).

Relatively few studies have characterized the variation of nonpoint-source contaminants associated with row crop agriculture, particularly pesticides and their degradates, in karst aquifers. Long-term monitoring of Big Spring, a large karst spring in Iowa, has showed that seasonal variation in nitrate is associated with infiltration recharge, while elevated atrazine concentrations can result from direct surface runoff into conduits in an aquifer (Hallberg *et al.*, 1984). Rowden *et al.* (1995) detected one of two degradates of the herbicide atrazine analyzed in samples from Big Spring in Iowa. The magnitude and variation of measured concentrations of the degradate generally were similar to those of atrazine. Hippe *et al.* (1994) sampled four springs in a regolith-mantled karst aquifer in Carlisle, Pennsylvania, for nutrients, atrazine, atrazine degradates, and two other pesticides roughly 25 times over a period of one year. Deethylatrazine (atrazine degradate) concentrations generally were twice as high as atrazine concentrations and varied considerably more. The ratio of deethylatrazine to atrazine suggested that much of the discharge from several of the springs was associated with slow movement through soils rather than recharge of surface runoff into sinkholes (Hippe *et al.*, 1994). Currens (1999) attributed low nitrate loads at Pleasant Grove Spring in Kentucky to storage of nitrate in the diffuse flow system and peak atrazine loads to field runoff entering the karst aquifer through swallets or sinkholes. Peterson *et al.* (2002) determined that about 75% of the nitrate in a spring moved through the regolith with successive recharge events in a mantled karst terrane.

As part of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program, a study was conducted between March 1999 and March 2001 to characterize the variation in water quality, particularly with respect to nitrate, pesticides, and selected pesticide degradates in two springs affected by agricultural-chemical use in the Mississippian Carbonate Aquifer in northern Alabama. The timing and total ranges of selected pesticide degradate concentrations relative to the parent pesticide was of particular interest because the occurrence of degradates is an important aspect of understanding the fate of pesticides in the environment. General water-quality data collected during the study were used in conjunction with nitrate and pesticide data to characterize how the hydrology of a subsoil (mantled) karst aquifer affects concentrations of these constituents in discharge from the springs.

STUDY AREA

The study area is in the Highland Rim section of the Interior Low Plateaus Physiographic Province in northern Alabama (Figure 1). The landscape can be characterized as subsoil karst (White, 1988); carbonate rocks of Mississippian age are overlain by regolith that was derived *in situ* by weathering. The surficial geologic units in the area are the Fort Payne Chert and the Tuscumbia Limestone, which are the principal water-bearing units of the Mississippian Carbonate Aquifer, the shallow aquifer throughout the Highland Rim. The Chattanooga Shale underlies the Fort Payne Chert and serves as a regional confining

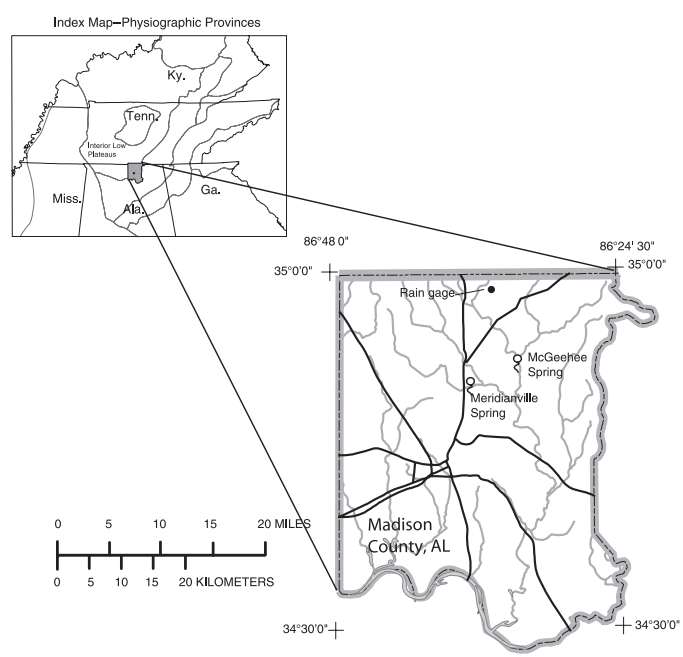

FIGURE 1. Location of Sampled Springs and Rain Gage in Madison County, Alabama.

unit limiting the movement of ground water from the Mississippian Carbonate Aquifer to deep, regional flow paths. In the areas near the springs, the depth to the Chattanooga Shale is about 20-40 m (Geological Survey of Alabama, 1975). Both formations contain considerable amounts of chert, particularly the Fort Payne Chert, which contains as much as 60% siliceous material (Stearns and Wilson, 1971). The geologic units are relatively flat lying to gently dipping. Topographic relief in the area generally is less than 30 m, but locally can be as much as 100 m. Karst features are present throughout the area, but are not abundant in the areas near the springs with the exception of several closed depressions that are about 1-3 km upgradient from Meridianville Spring. The relatively thick regolith and large amounts of siliceous material in the bedrock also tend to limit the development of sinkholes and moderate the surface expression of karst features. The regolith generally is between 5 and 25 m thick and consists of a mixture of clay, silt, and clay-sized chert, with some chert gravel and chert interbeds. Locally, portions of the regolith have been reworked.

Ground water in the Mississippian Carbonate Aquifer flows through solution openings along bedding planes, fractures, and joints in bedrock. Recharge to the aquifer is largely from infiltration of precipitation through the regolith, which is hydraulically connected to the underlying bedrock aquifer. Direct recharge to the aquifer also occurs from surface drainage into sinkholes and where water moves through macropores. Ground-water flow paths generally are relatively short, on the order of several kilometers, with resurgences to nearby streams, many small springs, and a few large springs (Brahana and Bradley, 1986). The depth to ground water in the Mississippian Carbonate Aquifer generally is less than 30 m. The aquifer is a significant source of water for domestic and public supply in northern Alabama and in parts of middle Tennessee.

The study area has a temperate climate with average annual precipitation of about 147 cm per year. Rainfall is fairly evenly distributed throughout most of the year, but the period from August through October tends to be drier, with greater depletion of storage, lower spring flow, and lower ground-water levels. Rainfall during the two-year study period was about 47 and 30 cm less than the average annual rainfall for each 12-month period.

Meridianville and McGeehee Springs are moderately sized springs with an average measured discharge of 122 and 17 l/s, respectively, that issue from the Fort Payne Chert and flow throughout the year. These springs were selected because of their proximity to agricultural land and the likelihood that the water quality would reflect this land-use activity. Soybeans, cotton, and corn are the principal crops grown in northern Alabama.

MATERIALS AND METHODS

Water samples were collected from McGeehee and Meridianville Springs roughly bimonthly between April 1999 and January 2000, and monthly between March 2000 and March 2001. No specific attempt was made to collect samples following storms, but some samples were collected within two to five days of relatively large rainfalls. Discharge from the springs was measured across a channel below the springs with a pygmy meter when the samples were collected. Hourly temperature data were collected using an Onset Computer Corporation Optic Stowaway temperature logger with an accuracy of ±0.2°C. In addition, hourly specific-conductance and temperature data for Meridianville Spring were collected for about 60 days from mid-February to mid-April 2001 with a Hydrolab MiniSonde 4a having an accuracy of ±1%. Hourly specific-conductance data were not collected at McGeehee Spring because the equipment could not be secured at this site. Daily rainfall data were obtained for the raingage at Hazel Green, Alabama, from Agricultural Weather Information Service, Inc., Auburn, Alabama. Samples for inorganic and nutrient analysis were filtered through a 0.45-μm capsule filter, and cations were preserved with 7.5 N nitric acid; pesticide samples were filtered through a 0.7-μm pore-size glass fiber filter and collected in baked amber glass bottles. Samples were chilled on ice and shipped for next-day delivery to the laboratory. Samples were analyzed using approved USGS analytical methods at the National Water-Quality Laboratory (NWQL) in Denver, Colorado, and at the USGS Organic Geochemistry Research Laboratory in Lawrence, Kansas. Dissolved inorganic constituents were determined at the NWQL using atomic absorption, inductively coupled plasma, ion-chromatography, ion specific electrode, and colorimetric methods, as described in Fishman and Friedman (1989) and Fishman (1993). Alkalinities were determined in the field at the time of sample collection using incremental titrations.

Two analytical methods were used at the NWQL to analyze 90 pesticides and 14 pesticide degradates. Pesticides were extracted from samples by pumping a liter of filtered sample through a disposable solid-phase extraction column containing octadecyl-bonded porous silica (C-18) (Zaugg *et al.*, 1995) for one method. Extracts from these columns were analyzed with gas chromatography/mass spectrometry

(GC/MS). For the second method, pesticides were extracted from filtered samples with a graphitized-carbon sorbent column and were analyzed using high-performance liquid chromatography/mass spectrometry (HPLC/MS) (Furlong *et al.*, 2001). Ten samples were collected from June 2000 to March 2001 for analysis of fluometuron degradates at the USGS Organic Geochemistry Research Laboratory in Lawrence, Kansas. These samples were filtered and extracted on a solid phase C-18 column. Extracts were analyzed by GC/MS. Methods for the fluometuron degradate analysis are described in Kish *et al.*, 2000.

The HPLC/MS and fluometuron degradate methods had not received final approval by the USGS Office of Water Quality at the time samples were analyzed. Although the analytical methods did not change following approval, data analyzed prior to method approval are considered provisional. Several of the samples submitted for HPLC/MS analysis collected in 1999 exceeded the recommended holding time. Concentrations of fluometuron in these samples that were stored refrigerated between 50 and 100 days may be biased low as a result of degradation in sample bottles during sample storage. Samples from Meridianville Spring on April 27, July 14, August 18, and October 26, 1999 and McGeehee Spring on April 26 and October 26, 1999, were the affected samples. The fluometuron data for these samples are summarized and plotted because a follow-up holding-time study by the NWQL estimated a half-life of fluometuron in sample bottles to be about 50 days in a ground-water matrix (Furlong *et al.*, 2003).

RESULTS AND DISCUSSION

Characterizing Ground-Water Flow to and From the Springs

Ground-water temperature data were collected hourly to help characterize the hydrology of the two springs. Differences in the temperature data indicate that the springs represent distinct flow regimes in the Mississippian Carbonate Aquifer. Ground-water temperatures at McGeehee Spring varied seasonally about 4°C (Figure 2), indicating that ground-water flow paths are relatively shallow. Spikes and dips in temperature following locally heavy rainfall indicate that a component of recharge follows short, direct flow paths from land surface to the spring. Based on the combination of seasonal and short-term fluctuations in the water temperature data, the average

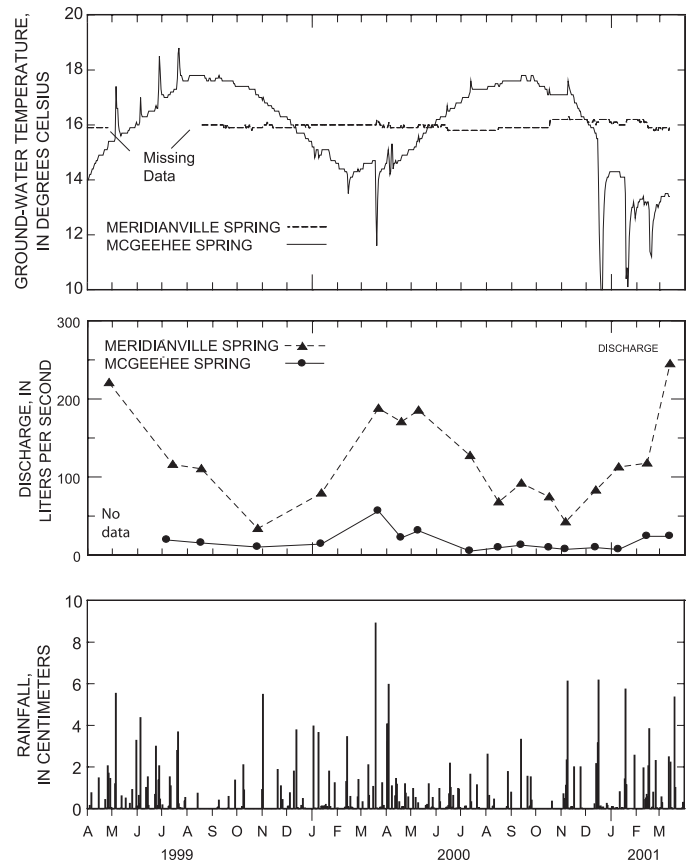

FIGURE 2. Hourly Ground-Water Temperature and Discharge Data for McGeehee and Meridianville Springs and Daily Rainfall.

residence time for ground water discharging from McGeehee Spring is probably relatively short. Ground-water temperatures at Meridianville Spring varied about 0.1°C during the period of record, indicating that the majority of the flow to this spring follows deeper and longer flow paths in the aquifer than water issuing from McGeehee Spring. Any contribution of recharge from shorter, direct flow paths following rainfall was small enough not to affect the temperature. Although diffuse flow likely is a component of the discharge at both springs, based on water temperature, Meridianville Spring seems to be dominated by diffuse flow. In addition, the flow from Meridianville Spring is considerably larger (Figure 2) indicating a larger contributing area with longer flow paths, and a larger ground-water reservoir for this spring all of which likely moderate changes in water temperature.

Water temperature did not fluctuate appreciably at Meridianville Spring during the study; however, continuous specific-conductance data collected from mid-February through mid-April 2001 indicate an increase in specific conductance of as much as 15% shortly after two rainfalls of about 4 cm or more

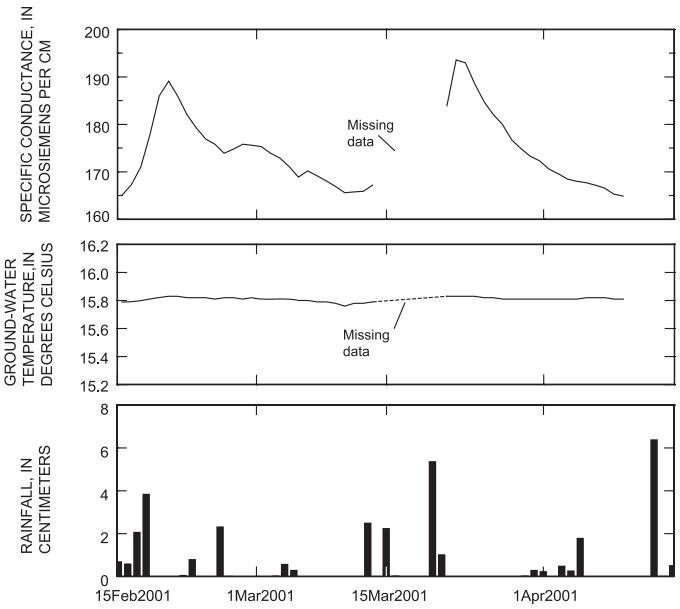

FIGURE 3. Hourly Specific-Conductance and Ground-Water Temperature Data for Meridianville Spring for the Period Mid-February Through Mid-April 2001.

(Figure 3). Smaller increases in specific conductance also occurred following other smaller storms. Continuous specific conductance data were not collected at McGeehee Spring because of site conditions at this spring. These increases in specific conductance are interpreted to be the result of water with high specific conductance being released from storage in the aquifer and moving to the spring in response to the hydraulic loading on the system from rainfall, as has been suggested for other karst aquifer springs (Ashton, 1966; Bakalowicz *et al.*, 1974; cited in Ford and Williams, 1989). In many karst springs, this initial increase in specific conductance is followed within hours or a few days by a decrease in specific conductance as low conductivity surface runoff moves into and through an aquifer to discharge at a spring (White, 1988; Ryan and Meiman, 1996). At Meridianville Spring, however, it appears that any contribution to flow from rapid movement of runoff into the aquifer after rainfall makes up a small portion of the spring discharge and has no discernible effect on the specific conductance or water temperature. The continuous specific-conductance data demonstrate that an important aspect of the response of karst springs to rainfall, the displacement of water from storage in the aquifer, cannot be characterized by interpreting temperature data alone.

In addition to continuous water-temperature and specific conductance data, variation in major ion concentrations were used to characterize the seasonal variation in geochemistry and residence time of ground water issuing from the two springs. Water

TABLE 1. Average Flow and Composition of Spring Discharge and Coefficient of Variation for Flow and Selected Water-Quality Constituents.

	McGeehee Spring	Meridianville Spring
Discharge (l/s)	17 (74)	122 (47)
Dissolved oxygen (mg/l)	6.3 (19)	8.3 (7)
pH	6.8 (4)	7 (2)
Specific conductance	125 (10)	166 (9)
Temperature (°C)	16.1 (11)	16.1 (1)
Hardness (mg/l as $CaCO_3$)	57 (12)	75 (6)
Calcium (mg/l)	17 (12)	25 (7)
Magnesium (mg/l)	3.5 (12)	3.4 (4)
Potassium (mg/l)	0.5 (49)	0.4 (16)
Sodium (mg/l)	1.1 (9)	2.1 (16)
Alkalinity (mg/l)	57 (15)	81 (10)
Chloride (mg/l)	2.8 (17)	3.5 (12)
Sulfate (mg/l)	2.5 (83)	1.8 (23)
Nitrate as N (mg/l)	2.3 (15)	2.7 (8)
Silica (mg/l)	7.3 (11)	8.2 (2)
SI_c	−1.7 (19)	−1.2 (15)
pCO_2	−2.01 (11)	−2.04 (7)
Fluometuron (μg/l)	0.5 (52)	0.4 (17)
Atrazine (μg/l)	0.009 (100)	0.011 (62)

Notes: $CaCO_3$, calcium carbonate; SI_c, calcite saturation index. Coefficient of variation is in parentheses and expressed as percent; data are available at http://waterdata.usgs.gov.

issuing from both springs is a calcium-bicarbonate type with total dissolved solids less than 120 mg/l, a pH of about 7.0 and dissolved-oxygen (DO) concentrations of about 7 mg/l. Concentrations of most major ions varied seasonally in both springs, with greater changes in concentration in samples from McGeehee Spring than from Meridianville Spring (Table 1). Inferred longer average ground-water residence time result in a smaller range of concentration for most constituents in Meridianville Spring compared to McGeehee Spring (Table 1).

Inorganic water-quality data indicate that flow paths or relative ground-water residence times of the water discharging from the springs differ during different parts of the year (Figure 4). The degree of saturation of ground water with respect to minerals such as calcite can be used as a qualitative indicator of the time that water has been in contact with carbonate aquifer material. The calcite saturation index (SI_c) was calculated for all samples using the water-quality program PHREEQC (Parkhurst and Appelo, 1999). Water in both springs is under saturated with respect to calcite, but water discharging from Meridianville Spring had a higher SI_c throughout the year than water from McGeehee Spring. The amount of variation in the SI_c was somewhat lower than in McGeehee Spring. The relatively large amount of chert in the Fort Payne Chert may keep the concentrations of bicarbonate, calcium, and magnesium low in water from both springs because much of the

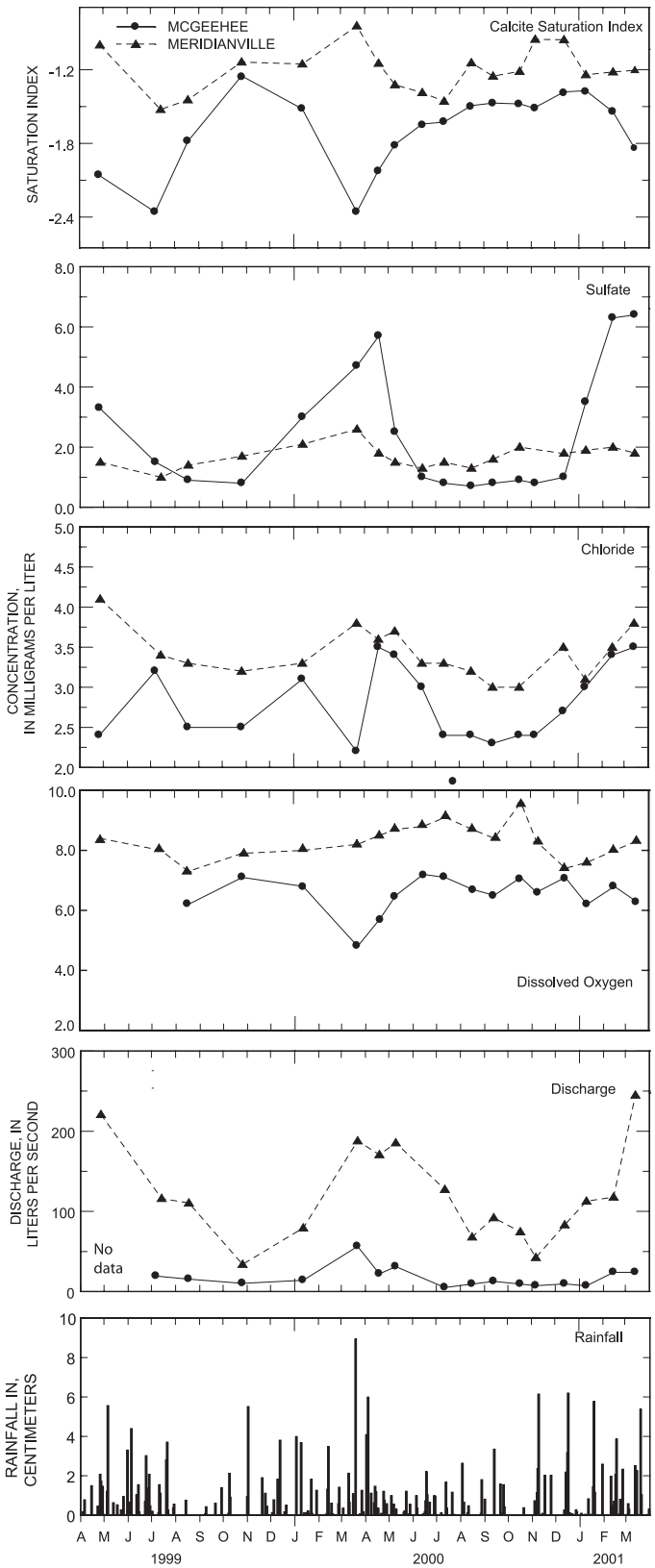

FIGURE 4. Discharge, Calcite Saturation Index, Sulfate, Chloride, and Dissolved Oxygen Data for McGeehee and Meridianville Springs and Nearby Rainfall.

surrounding carbonate material has been dissolved, and ground water may be in contact with residual chert rather than limestone.

Although local differences in aquifer lithology could account for some of the difference in SI_c between the two springs, changes in SI_c over time probably represent differences in the average ground-water residence times in the aquifer for discharge from the two springs. At McGeehee Spring, the SI_c decreased following increases in recharge from about November to March as indicated by an increase in discharge for the same periods (Figure 4). The SI_c increased from a low of about −2.4 in March 2000 when discharge was greatest to higher values during the summer when discharge was low and consisted predominantly of ground water with longer residence times. The SI_c did not decrease until about January 2001 when discharge began to increase (Figure 4).

In contrast to McGeehee Spring, the increase in recharge from about November to March resulted in an increase in the SI_c at Meridianville Spring. This response is analogous to the increase in specific conductance observed with the hourly data collected at Meridianville Spring (Figure 3). Hydraulic loading on the ground-water system from rainfall, illustrated by the large rainfall in March 2000, appears to induce the flow of ground water with longer residence times in storage in the aquifer to the spring resulting in discharge of water having the highest SI_c. Following this recharge event, dissolved oxygen increased from 8.2 to 9.1 mg/l between March and July 2000, supporting the interpretation that the portion of water with short residence time increased. From about July to November when discharge is low, the portion of discharge with longer residence times in the aquifer increases in both springs as indicated by elevated SI_c.

Other constituents contributed to ground water as a result of water-rock interaction generally had similar concentration profiles to the SI_c, but sulfate and chloride concentration profiles differed from the SI_c at both springs (Figure 4). These constituents generally were at their maximum from about November to March, when discharge is high at both springs (Figure 4), indicating that these constituents are contributed to ground water in greater concentrations with infiltration recharge. The amount of variation in chloride and sulfate was greater in samples from McGeehee Spring than from Meridianville Spring. Low concentrations of chloride in samples from McGeehee Spring collected in April 1999 and March 2000 are interpreted to be the result of short-term dilution from rainfall. These two samples were collected within a few days of rainfall and were turbid suggesting rapid recharge to the aquifer from surface runoff to conduits. Decreases in hardness, alkalinity, and

silica in these samples, further indicate dilution of ground water from the movement of surface runoff into the aquifer. Sulfate concentrations did not decrease in these two samples, indicating sulfate is transported to the aquifer both through slow infiltration and rapid recharge pathways.

The conceptualization of the hydrology of these springs based on the water temperature and inorganic constituents is that flow to both springs is a combination of diffuse and conduit flow. Comparatively, Meridianville Spring can be characterized as a predominantly diffuse-flow system with a longer average ground-water residence time with greater storage of water in the overlying regolith and in the aquifer compared to McGeehee Spring. Following periods of recharge, water moves from storage in the regolith and aquifer, and this water is a significant component of flow at Meridianville Spring. At McGeehee Spring, rapid recharge and discharge of water to the aquifer occurs from surface runoff to conduits. This type of recharge appears to be a small component of flow at Meridianville Spring; however, increases in chloride and flow at both springs between November and March indicate that a component of the flow at both springs is water with relatively short residence times that has moved into the aquifer as slow infiltration recharge.

Variation of Nitrate in Spring Discharge

Nitrate is one of the most widespread ground-water contaminants and is of particular concern in karst aquifers (Hallberg and Keeney, 1993). Nitrate concentrations varied seasonally in samples from both springs, but concentrations generally were between 2 and 3 mg/l, as N (Figure 5). These concentrations are considerably lower than the USEPA maximum contaminant level for drinking water of 10 mg/l, but probably represent elevated concentrations in the aquifer. Based on a relation between land use and nitrate concentrations, Kingsbury and Shelton (2002) suggested that background concentrations of nitrate in the Mississippian carbonate aquifer are less than 1 mg/l based on a random sample of about 30 wells throughout the Eastern Highland Rim. Likely sources of nitrate are fertilizer and animal-waste application to cropland because agriculture is the dominant land use in the area around the springs.

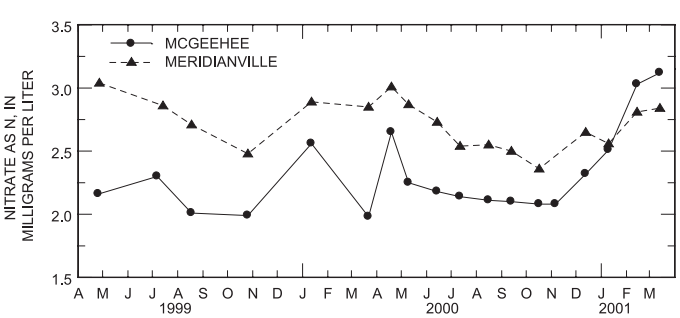

FIGURE 5. Nitrate Concentrations in Samples From McGeehee and Meridianville Springs.

The variation in nitrate concentration is similar to other inorganic constituents (Table 1) because nitrate also is largely contributed to the aquifer as a result of the infiltration and movement of water through the soil and unsaturated zone. The range in nitrate concentrations at McGeehee Spring was greater than at Meridianville Spring, and changes in nitrate concentrations are similar to changes in chloride and sulfate at both springs (Figure 4). Low nitrate concentrations in samples from McGeehee Spring in April 1999 and March 2000 (Figure 5) most likely result from short-term dilution by surface runoff moving into the aquifer, similar to the change seen for chloride. The seasonal variation in nitrate and other inorganic constituent concentrations indicate that a component of discharge from both springs has relatively short residence times in the aquifer.

Ground-water nitrate concentrations are affected by a number of factors including the source of nitrogen, variation over time of source inputs such as fertilizer application, transformation processes such as denitrification, and uptake by plants and crops. Given that chloride is a conservative ion in ground-water systems, and chloride and nitrate concentrations are similar at both springs, nitrate appears to be largely conserved along the ground-water flow paths for these springs. The similarity in concentration profiles for nitrate, chloride, and sulfate indicates that these constituents are contributed in large part from surface or near-surface sources and similar processes affect their concentrations in the aquifer.

Increases in nitrate concentration at both springs from November to April (Figure 5) most likely result from increased recharge rates to the aquifer. The amount of leachable nitrate probably increases during the fall because of optimal (warm and moist) soil conditions for nitrification of soil organic-N (Addiscott, 1996) and decreased N uptake as a result of crop harvest. The similarity in nitrate, chloride, and sulfate concentration profiles, however, indicates that recharge is the principal factor affecting nitrate concentration. During the summer, when evapotranspiration is high and recharge rates are low, discharge from the springs consists predominantly of ground water having long residence times and low nitrate concentrations. In the fall when recharge increases, nitrate in the soil zone is transported to the ground-water system.

Variation of Pesticides and Pesticide Degradates in Spring Discharge

Pesticide and pesticide degradates were detected frequently in low concentrations in samples collected from both springs. Samples were analyzed for 93 pesticides and 19 pesticide degradates. Of these, 29 pesticides or degradates were detected at least once with degradates accounting for 31% of the pesticides detected. All detections were at concentrations less than 1 $\mu g/l$, and only a few pesticides or degradates were detected in most samples. Atrazine, fluometuron, and their degradates were detected throughout the study in samples from both springs (Figure 6). Fluometuron, a herbicide used predominantly for cotton cultivation, was the pesticide detected most frequently and at the highest concentrations in samples from both springs. Athough the fluometuron degradate demethylfluometuron (DMFM) was only analyzed in samples collected beginning in June 2000, DMFM was detected in every sample and generally at concentrations similar to fluometuron.

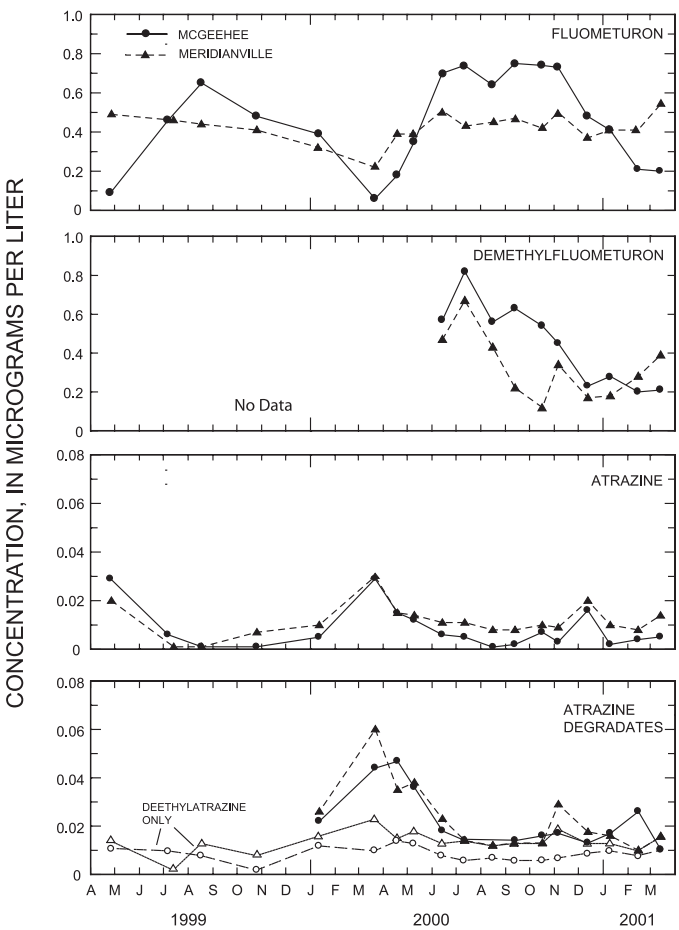

FIGURE 6. Concentrations of Fluometuron, Atrazine, and Their Degradates in Samples From McGeehee and Meridianville Springs.

Sustained concentrations of fluometuron in both springs throughout the hydrologic cycle (Figure 6) indicate that residual fluometuron persists in the soil and unsaturated zone or is stored within the aquifer throughout the year. Fluometuron concentrations in samples from Meridianville Spring varied only slightly seasonally (Figure 6) and had a coefficient of variation comparable to several inorganic constituents (Table 1). Fluometuron concentrations in samples from McGeehee Spring, however, varied seasonally, with low concentrations from about December to May and high concentrations from June to November (Figure 6). During the summer and fall of 2000, concentrations of fluometuron in samples from McGeehee Spring remained high for six months before beginning to decrease in November (Figure 6). Fluometuron concentrations in samples from McGeehee Spring were inversely correlated to discharge. Because of the relatively small amount of variation in concentrations of fluometuron in samples from Meridianville Spring, there generally was no correlation with discharge at Meridianville Spring with the exception of a decrease in concentration corresponding to the large rainfall in March 2000.

In contrast to fluometuron concentrations, DMFM concentrations decreased through the summer of 2000 at both springs (Figure 6). Of the three degradates of fluometuron analyzed, only DMFM was detected regularly. Trifluoromethylaniline (TFMA) was detected at concentrations near its reporting level (0.05 $\mu g/l$) in three samples from McGeehee Spring between September and November 2000, and trifluoromethylphenylurea, which had a higher method detection limit (0.32 $\mu g/l$), was not detected in any samples. The frequent detection of fluometuron and DMFM, few detections of TFMA, and no detections of trifluoromethylphenylurea during this study is similar to results for samples collected from three streams in the Mississippi Delta (Coupe *et al.*, 1998). DMFM concentrations were highest and comparable to or greater than fluometuron concentrations during June and July, but generally decreased through the summer to about half of the fluometuron concentration in December (Figure 6). The decrease in DMFM concentrations in both springs during the summer indicates that in fluometuron degradation rates decrease. Mueller *et al.* (1992) determined that degradation rates for both fluometuron and DMFM decreased with increasing depth in the subsurface in soils of the Mississippi River delta region. The movement of fluometuron deeper into the soil profile following its application and subsequent rainfall may result in a decrease in degradation rates of fluometuron. In this study, the increase in DMFM concentration at Meridianville Spring and leveling off in concentration at McGeehee Spring from about

January to March 2001 indicates that increases in recharge in the late winter and early spring mobilize DMFM that has formed in the soil and unsaturated zones during the summer and fall.

The amounts of fluometuron and DMFM transported from about January to March are comparable to or greater than the amounts transported shortly after the application period during the growing season, particularly at Meridianville Spring. Instantaneous loads of fluometuron and DMFM (Figure 7) were calculated to characterize the transport of these compounds in the aquifer. At Meridianville Spring, long average ground-water residence times moderate the variation in fluometuron concentrations, but loads of fluometuron have a discernible seasonal variation. Increases in fluometuron loads in Meridianville Spring generally correspond to increases in discharge, and the largest instantaneous load was in March 2001 (Figure 7), about a month before fluometuron typically is applied to fields. Hippe *et al.* (1994) noted a similar variation in loads of atrazine and its degradates for springs sampled in Pennsylvania. DMFM loads varied similarly to fluometuron loads at both springs, but the difference between the maximum and minimum loads were greater than for fluometuron in Meridianville Spring. At McGeehee Spring, changes in fluometuron and DMFM loads generally were smaller than at Meridianville Spring and loads show a slight seasonal variation (Figure 7). The shallow flow system contributing to McGeehee Spring likely has a thin unsaturated zone with less residual fluometuron per unit area resulting in a smaller increase in fluometuron and DMFM loads than at Meridianville Spring when recharge increases. The deeper ground-water system at Meridianville Spring conversely allows for more storage of fluometuron per unit area in the unsaturated and diffuse flow zones.

Atrazine and its degradates were detected at low concentrations throughout the study, and changes in concentration over time were similar in both springs (Figure 6). The highest concentrations in samples

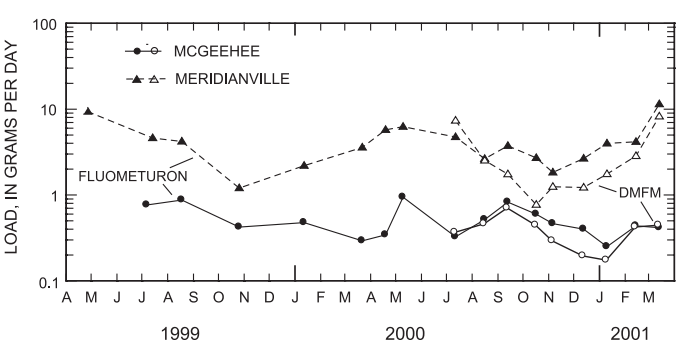

FIGURE 7. Instantaneous Loads of Fluometuron and Demethylfluometuron (DMFM) in Samples From McGeehee and Meridianville Springs.

from both springs occurred in March and April 2000, and concentrations decreased by approximately half with the next monthly sample. Atrazine concentrations were at a minimum from about July to September; atrazine was not detected in the August sample from both springs in 1999, and only in the sample from Meridianville Spring during 2000. Atrazine concentrations in both springs were correlated to discharge. Peak concentrations of atrazine and its degradates coincided with peak discharges, so variation in instantaneous loads for these compounds was similar to the variation in their concentration.

The principal degradate of atrazine detected was deethylatrazine (DEA), which typically made up about 50% of the total degradate concentration. DEA concentrations did not vary appreciably throughout the year (Figure 6). The increase in the total degradate concentration during the spring of 2000 is the result of detections of hydroxyatrazine, deisopropylatrazine (DIA), and deethyldeisopropylatrazine, which were not detected later in the summer. Hydroxyatrazine was detected in 15% of the samples from Meridianville Spring but was present in 60% of samples collected from McGeehee Spring. DIA is a degradate typically associated with surface water and not commonly detected in ground water (Plummer *et al.*, 1993). This degradate was detected in only three samples that were collected in March and April when discharge (and recharge) was highest for both springs. Deethyldeisopropylatrazine was detected in about half of the samples at both springs and generally was not detected during the summer when discharge was lowest. The total concentration of atrazine degradates usually was greater than atrazine in samples from both springs.

The solubility, sorption coefficient, and half-life of atrazine and fluometuron are comparable (USDA, 2006); yet the concentration profiles differ markedly. Differences in the amounts of these pesticides applied in the contributing areas of the springs may account for some of the variability between the profiles. Cotton has a long growing season with up to three applications of fluometuron. Cotton has a long growing season with up to three applications of fluometron. In the areas near the spring, cotton fields are more prevalent than corn, the primary crop for atrazine use. The difference in concentration profiles also may be the result of differences in fate and transport of these pesticides. Drier soil conditions during the time frame in which fluometuron is applied (April-July) compared to when atrazine is applied (March-May) may allow a greater infiltration of fluometuron into the soil and less movement with runoff compared to atrazine.

Concentration ratios of atrazine to DEA also indicate that transport of atrazine to the aquifer differs from fluometuron. Samples from both springs with

the highest concentrations of atrazine also had a DEA to atrazine ratio (DAR) of less than 1, indicating that the short-term peak atrazine concentrations in the aquifer are related to rapid movement of water into the aquifer through direct recharge. The DAR has been used as a qualitative indicator of the pathway that water and atrazine move through the subsurface (Adams and Thurman, 1991). DEA forms from the breakdown of atrazine by microbes in the soil environment. A DAR less than 1 may indicate rapid transport to the subsurface with short residence times for water and atrazine in the soil zone. At McGeehee Spring, the highest atrazine concentrations are inversely correlated with the SI_c, which supports the interpretation that maximum concentrations of atrazine are associated with rapid movement of water from the surface to the aquifer. In contrast, maximum atrazine concentrations at Meridianville Spring (April 1999, March and December 2000) coincide with high SI_c (Figures 4 and 6). A low DAR for these samples indicates rapid movement of atrazine and water into the subsurface, but an increase in SI_c indicates the movement of water from storage in the aquifer. These apparently contradictory results indicate that a small portion of rapid recharge with elevated atrazine concentrations mixes with the water released from storage in the aquifer such that water temperature and inorganic water quality are not affected appreciably, but atrazine concentrations increase.

SUMMARY AND CONCLUSIONS

The objective of this study was to characterize and compare the variation of nitrate and selected pesticides and pesticide degradates by evaluating water quality in two springs representing distinct flow regimes in the Mississippian Carbonate Aquifer in northern Alabama. Inorganic water-quality data were used to help characterize the geochemistry and relative residence time for ground-water discharge from the springs seasonally. The longer average residence time for ground-water discharging from Meridianville Spring appears to be the primary cause for relatively low variations in water quality compared to water that follows shallower and shorter flow paths from McGeehee Spring. In both springs, concentrations of most constituents vary less than flow, and changes in water quality associated with relatively rapid recharge from surface runoff moving into the aquifer have a short duration. Although inorganic water-quality data for the two springs indicate a different hydrologic response to rainfall, the seasonal variation of the nonpoint source contaminants such as nitrate and pesticides generally is similar for the two springs.

An increase in ground-water recharge from about November to March facilitates the transport of nitrate and some pesticides and their degradates that are present in the soil and unsaturated zone or are present in storage in the aquifer. Soil nitrate concentrations probably increase in the fall as a result of nitrification of soil organic nitrogen, reduced uptake by plants, and crop harvest, but the similarity of chloride and nitrate concentrations indicates that an increase in recharge is the dominant mechanism for the increase in nitrate concentrations in the winter. During the summer when evapotranspiration is highest and recharge rates are lowest, the flow from the springs consists predominantly of ground-water storage in the aquifer, and nitrate concentrations are lower. The seasonal variation in nitrate and pesticide concentrations indicates that a component of discharge from both springs has relatively short residence times in the aquifer.

The seasonal pulse of pesticides in surface water that results from their use on cropland during the growing season is well documented in numerous studies. The fluometuron data collected for this study, however, indicate that seasonal variation in the amount of recharge to ground-water systems has implications for transport of pesticides that move into aquifers with infiltration recharge. Pesticides and their degradates also may be transported to and discharged from aquifers several months after the growing season as a result of an increase in recharge during the fall and winter months.

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LITERATURE CITED

Adams, C.D. and E.M. Thurman, 1991. Formation and Transport of Deethylatrazine in the Soil and Vadose Zone. Journal of Environmental Quality 20(3):540-547.

Addiscott, T.M., 1996. Fertilizers and Nitrate Leaching. *In*: Agricultural Chemicals and the Environment, R.E. Hester and R.M. Harrison (Editors). Royal Society of Chemistry, Cambridge, United Kingdom, Information Services, 5, pp. 1-26.

Ashton, K., 1966. The Analysis of Flow Data From Karst Drainage Systems. Transaction of Cave Research Group, Great Britain 7(2):161-203.

Bakalowicz, M., B. Blavoux, and A. Mangin, 1974. Apports du Tracage Isotopique Naturel a la Connaissance du Fonctionnement D'un Systeme Karstique-Teneurs en Oxygene-18 de Trois Systemes des Pyrenees, France. Journal of Hydrology 23:141-158.

Brahana, J.V. and M.W. Bradley, 1986. Preliminary Delineation and Description of the Regional Aquifers of Tennessee – The Highland Rim Aquifer System. U.S. Geological Survey Water Resources Investigations Report 82-4054, 38 pp., Nashville, Tennessee. http://pubs.usgs.gov/wri/wri824054/, *accessed* May 2007.

Coupe, Jr., R.H., E.M. Thurman, and L.R. Zimmerman, 1998. Relation of Usage to the Occurrence of Cotton and Rice Herbicides in Three Streams of the Mississippi Delta. Environmental Science and Technology 32(23):3673-3680.

Currens, J.C., 1999. Mass Flux of Agricultural Nonpoint-Source Pollutants in a Conduit-Flow-Dominated Karst Aquifer, Logan County, Kentucky. Kentucky Geological Survey, Report of Investigations 1, 151 pp., Lexington, Kentucky.

Fishman, M.J. (Editor), 1993. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments. U.S. Geological Survey Open-File Report 93-125, 217 pp. http://pubs.er.usgs.gov/usgspubs/ofr/ofr93125, *accessed* May 2007.

Fishman, M.J. and L.C. Friedman (Editors), 1989. Methods for Determination of Inorganic Substances in Water and Fluvial Sediments. U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chap. A1, 545 pp. http://pubs.usgs.gov/twri/, *accessed* May 2007.

Ford, D.C. and P.W. Williams, 1989. Karst Geomorphology and Hydrology. Unwin Hyman Limited, London, United Kingdom, 601 pp.

Furlong, E.T., B.D. Anderson, S.L. Werner, P.P. Soliven, L.J. Coffey, and M.R. Burkhardt, 2001. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of Pesticides in Water by Graphitized Carbon-Based Solid-Phase Extraction and High-Performance Liquid Chromatography/Mass Spectrometry. U.S. Geological Survey Water Resources Investigations Report 01-4134, 73 pp., Denver, Colorado.

Furlong, E.T., J. Blomquist, and R.J. Gilliom, 2003. Data-Reporting Conventions and Implications for Interpreting Results From Custom Method 9060 for Samples Collected From March 1, 1999, to December 31, 1999. U.S. Geological Survey National Water Quality Laboratory Technical Memorandum 03.01, http://nwql.usgs.gov/Public/tech_memos/nwql.2003-01.html, *accessed* May 2007.

Geological Survey of Alabama, 1975. Environmental Geology and Hydrology Huntsville and Madison County, Alabama. Geological Survey of Alabama Atlas Series 8, 118 pp., Tuscaloosa, Alabama.

Hallberg, G.R. and D.R. Keeney, 1993. Nitrate. *In*: Regional Ground-Water Quality, W.M. Alley (Editor). Van Nostrand Reinhold, New York, New York, pp. 297-322.

Hallberg, G.R., R.D. Libra, E.A. Bettis III and B.E. Hoyer, 1984. Hydrogeologic and Water Quality Investigations in the Big Spring Basin, Clayton County, Iowa. Iowa Geological Survey Open-File Report 84-4, 231 pp., Iowa City, Iowa.

Hippe, D.J., E.C. Witt, and R.M. Giovannitti, 1994. Hydrogeology, Herbicides and Nutrients in Ground Water and Springs, and Relation of Water Quality to Land Use and Agricultural Practices Near Carlisle, Pennsylvania. U.S. Geological Survey Water-Resources Investigations Report 93-4172, 66 pp, Lemoyne, Pennsylvania. http://pubs.er.usgs.gov/usgspubs/wri/wri934172, *accessed* May 2007.

Jacobson, R.L. and D. Langmuir, 1974. Controls on the Quality Variations of Some Carbonate Spring Waters. Journal of Hydrology 23:247-265.

Kingsbury, J.A. and J.M. Shelton, 2002. Water Quality of the Mississippian Carbonate Aquifer in Parts of Middle Tennessee and Northern Alabama, 1999. U.S. Geological Survey Water-Resources Investigations Report 02-4083, 36 pp., Nashville, Tennessee. http://pubs.usgs.gov/wri/wri024083/, *accessed* May 2007.

Kish, J.L., E.M. Thurman, E.A. Scribner, and L.R. Zimmerman, 2000. Methods of Analysis by the U.S. Geological Survey Organic Geochemistry Research Group–Determination of Selected Herbicides and Their Degradation Products in Water Using Solid-Phase Extraction and Gas Chromatography/Mass Spectrometry. U.S. Geological Survey Open-File Report 00-385, 13 pp., Lawrence, Kansas. http://ks.water.usgs.gov/Kansas/pubs/reports/ofr.00-385.html, *accessed* May 2007.

Mueller, T.C., T.B. Moorman, and C.E. Snipes, 1992. Effect of Concentration, Sorption, and Microbial Biomass on Degradation of the Herbicide Fluometuron in Surface and Subsurface Soils. Journal of Agricultural and Food Chemistry 40:2517-2522.

Parkhurst, D.L. and C.A.J. Appelo, 1999. User's Guide to PHREEQC (Version 2) a Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 pp., Lakewood, Colorado. http://pubs.er.usgs.gov/usgspubs/wri/wri994259, *accessed* May 2007.

Peterson, E.W., R.K. Davis, J.V. Brahana, and H.A. Orndorff, 2002. Movement of Nitrate Through Regolith Covered Karst Terrane, Northwest Arkansas. Journal of Hydrology 256:35-47.

Plummer, N.L., R.L. Michel, E.M. Thurman, and P.D. Glynn, 1993. Environmental Tracers for Age Dating Young Ground Water. *In*: Regional Ground-Water Quality, W.M. Alley (Editor). Van Nostrand Reinhold, New York, New York, pp. 255-294.

Quinlan, J.F., 1989. Ground-Water Monitoring in Karst Terranes: Recommended Protocols, Regulatory Problems, and Implicit Assumptions. U.S. Environmental Protection Agency, EPA/600/X-89/050, 79 pp., Las Vegas, Nevada.

Rowden, R.D., R.D. Libra, G.R. Hallberg, and B.K. Nations, 1995. Groundwater Monitoring in the Big Spring Basin 1992-1993: A Summary Review. Iowa Geological Survey Technical Information Series 34, 43 pp.

Ryan, M. and J. Meiman, 1996. An Examination of Short-Term Variations in Water Quality at a Karst Spring in Kentucky. Ground Water 34(1):23-30.

Scanlon, B.R., 1990. Relationships Between Groundwater Contamination and Major-ion Chemistry in a Karst Aquifer. Journal of Hydrology 119:271-291.

Shuster, E.T. and W.B. White, 1971. Seasonal Fluctuations in the Chemistry of Limestone Springs: A Possible Means for Characterizing Carbonate Aquifers. Journal of Hydrology 14:93-128.

Stearns, R.G. and J.M. Wilson, 1971. Petrography and Weathering of Silicastone of the Fort Payne Chert. The Journal of the Alabama Academy of Science 42(3):167.

USDA (U.S. Department of Agriculture), 2006. The ARS Pesticide Properties Database. http://www.ars.usda.gov/Services/docs.htm?docid=14199, *accessed* February 2008.

White, W.B., 1988. Geomorphology and Hydrology of Karst Terrains. Oxford University Press, New York, New York, 464 pp.

Zaugg, S.D., M.W. Sandstrom, S.G. Smith, and K.M. Fehlberg, 1995. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of Pesticides in Water by C-18 Solid-Phase Extraction and Capillary-Column Gas Chromatography/Mass Spectrometry With Selected-ion Monitoring. U.S. Geological Survey Open-File Report 95-181, 49 pp., Denver, Colorado. http://nwql.usgs.gov/Public/pubs/OFR95-181/OFR95-181.html, *accessed* May 2007.